

# ADVANCED TECHNIQUES FOR FABRICATING GOOD QUALITY GRAPHENE

## Abstract

From the last few decades, graphene and its derivatives have been a great deal of attention of researchers due to its remarkable chemical and physical properties. The defect free graphene possesses properties like high intrinsic mobility, good thermal conductivity and some excellent elasticity. The large specific surface area gives it an upper advantage in catalytic application and also, in some cases, in environmental remediation. Thus, it would be interesting to understand the different synthetic attributes of this novel material for small scale as well as industrial applications. It would be interesting to understand the different synthesis approaches in terms of small scale as well as industrial point of view as surface property and morphology has a profound influence on property of graphene sheets. The present article focuses mainly on the different approaches of fabrication of graphene and elaborates and explains the available existing techniques both fundamental as well as advanced approaches with broad classification (in terms of top down and bottom-up point of views) to corresponding subcategories, so as to impart the reader accurate idea regarding their usefulness in appropriate fields.

**Keywords:** Synthesis of graphene, top-down, bottom-up, mechanical exfoliation, intercalation, pyrolysis, radiation-based methods, reduction of graphite oxide, chemical methods.

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## I. INTRODUCTION

Owing to a great deal of novel properties, graphene has been in to the limelight from last decades. To separate the layers of graphene, the interactive “van der Waals” interactions need to be overcome [1-3]. Among different reported methods the synthesis are broadly of two types (1) the “top-down” approach and (2) “bottom-up” approach. In “top-down” approach involves tediousness in synthesis as well as low yield. On the other hand, the bottom-up method is verily suitable for different forms of graphene, with high purity, such as “nano-ribbons” and “graphene dots (so-called nanoflakes)” [4,5]. Conventional methods like CVD, micromechanical cleavage etc. In addition, the excess amount of time consumed for such fabrications keeps on hindering the voyage of its full exploration [6]. In this regard exfoliation (another alternative to micromechanical path) is highly economic and produces good yield [7].

These are examples of top-down methods where graphite (or any other precursor of graphene) is stripped down to graphene by chemical, physical, mechanical and thermal approaches [8, 9]

- 1. Method of Pyrolysis:** The pyrolysis process is widely followed for scaling up of graphene. In this method suitable percentage of sodium and ethanol are mixed which is subsequently heated in a airtight vessel above  $200^{\circ}\text{C}$  for 3 days [10,11]. This forms a precursor, which when pyrolyzed rapidly, results in graphene sheets [12-15], of  $0.1\text{ gmm}^{-1}$  [16]. Graphene of such quality are used in high density supercapacitor applications [17].
- 2. Method of Intercalation of Graphite:** Well exfoliated graphene sheets can be achieved by intercalation of different chemical species as intercalant. Here the distance between the sheets of carbon network in graphite increased and can change the property of graphene. Depending on the necessities, different intercalants can be chosen to exfoliate the graphene sheets to different extent, to make it useful in different fields like electrical, magnetic, thermal applications [13,14].
- 3. Slicing of Nanotube:** Good quality graphene nanoribbons (few microns) can also be synthesized using carbon nanotubes as precursor [10]. Different methods to achieve this are plasma etching [14] where the nanotubes are placed in an oxidizing solution such as acidified potassium permanganate. The quality of the product can be improved by such slicing method [15]. Nanotubes can be abraded between two stacked glass surfaces under a pressure of  $0.06\text{ N/cm}^2$ , resulting in high friction by which nano tubes are sliced to yield high quality graphene. Indeed, this method is very suitable in terms of quality and purity as no chemical modification is used and purity of the product is maintained.
- 4. Mechanical Exfoliation:** Mechanical exfoliation has high applicability due to its capabilities in forming high quality graphene films of lower size than tens micrometers from its precursors and hence it is considered to be one of the important techniques to produce high quality graphene sheets. However, this method is not suitable for mass production as thickness of thus obtained graphene is non-uniform. Also, the production cost is very high as the yield is very low. The widely used method for mechanical exfoliation is ‘scotch tape’ method where graphene sheets are peeled off from the corresponding graphite. In other words, graphite is alleviated micromechanically and repeatedly to split up and hence produce thin pieces of graphene. The optically

transparent films are then dissolved in acetone and studied under electron microscope or atomic force microscope, to analyze surface morphology. It has to be noted that ordinary visible light cannot be used for this purpose as the wavelength of visible light is much higher than the dimension of graphene sheets. In this regard electron microscopy, has successfully been used owing to the magnification of the order of  $10^5$  can be achieved. It was believed that the 'free-standing atomic planes' does not exist [4] as this type of structures are highly unstable if scaled down to nanometer range [9]. However, with later modification, flakes of sizes larger than 1 mm could be obtained [9]. Another technique used for mechanical exfoliation is ultrasonic oscillation, where diamond edge is used to 'scrape off' the graphene sheets from graphite, which is identical to the method of removal of graphene from crude carbon. However, the important advantage of this method is the control frequency of oscillation and contact pressure is possible, which induces uniform properties of the graphene sheets. Nano horns like structure around the edge of graphene has been successfully prepared by Jayasena et al. by this method. One of the major disadvantages of this method is that, it cannot be used for scaling up purpose. Usually N-methyl-2-pyrrolidone, sodium chlorate etc has been used as stabilizing liquid with a local shear rate of around  $10^3 \text{ s}^{-1}$ . This method successfully replaces the sonication method and hence low power consuming one, along with formation of defect-free and pure graphene. However, the properties of graphene sheets thus obtained is similar to that obtained in sonication method. With the use of proper solvents and surf acting agents, suitable quality of graphene can be manufactured in industrial scale.

- 5. Reduction of Graphite Oxide (GO):** Graphite nanoflakes can easily be obtained by reducing chemically graphene oxide. Thus, obtained graphene can suitably use in electrodes sensors, supercapacitors, fillers in polymers, paints etc. In this method a lower degree of exfoliation can be achieved [16, 17]. Although it can be exfoliated by sonication in appropriate solvents for example water, but the materials most of the times are electrically bad conductor or insulator. Thus, so as to restore its conductivity, it has to be reduced through thermally or chemically. High yields of graphene can also be produced by rapid heating [18]. It has been reported that using the paper making techniques, monolayer flakes of carbon with strong bindings can be achieved which are termed as graphene oxide paper with very high tensile module [19]. The membranes of graphene or its bases are impermeable to fluids excepting water [20]. Graphene oxide has been successfully be reduced under mild condition in acidic medium at ordinary conditions [21,22]. In addition, bacteria mediated approaches have also be used with the help of biomass to reduce graphene oxide. This involves bacteria incubating for a day at 130 rpm and 40 degreesCelsius and centrifuging the culture at ten thousand revolutions per minute to obtain the required biomass. 0.2 g of this biomass is added to the graphene oxide dispersion stirred for 3 days at 40 deg. However, graphene obtained in these methods contain lots of surface defects and is of highly impure.

Different synthetic approaches have been reported using "graphene oxide" as a "precursor" where the precursor starts getting reduced at high temperatures (as high as up to 1500 degrees) and pressure. Such a treatment also addressed as "solvothermal" or "hydrothermal" and helps to form graphene of high crystalline order, as high temperature and pressure reduces the graphene oxide in to the formation of "graphene sheets" of few layered dimensions. The use of high pressure further helps in fabrication in terms of reduction as well as improvement in surface properties [12].

- 6. Exfoliation by Electrochemical Methods:** For exfoliation of graphene, some interesting electrochemical methods are also employed, where 0.1 M sulphuric solution is used as electrolyte. Graphite flakes and platinum wire are used anode and cathode respectively, under a voltage of 10 V. Here graphite flakes start to dissolve and graphene sheets can be obtained, which are dispersed in dimethyl formamide. Such one-pot method for exfoliation also has been used for synthesis of high-quality graphene. In this method [BMIn][BF<sub>4</sub>] is used under static potential of 15V where graphene sheets are obtained which is subsequently washed in water and alcohol to get good quality graphene sheets.
- 7. Method of Sonication:** In sonication method good quality and oxygen free graphite and graphene can be obtained [23]. This is an example of top-down approach as ultrasonic energy has been used to achieve the separation of the graphene layers stacked together in the precursor, which has high usability in polymers. As this method utilizes sonication, it may be a matter of concern as sonication utilizes lots of amount of energy [11]. Here N-methyl-pyrrolidone can be used for dispersal of graphene and the method is useful in vacuum filtration, solvent casting, drop casting, spray coating [23]. However, power consumption is a great challenge in this method as already stated. In this regard, widely used solvent is TEA (Triethanol amine) which separates graphene from graphite [49-51]. A yield of more than 70% and thickness of about 1 nm can be achieved in this method. Such high-quality graphene possesses a conductivity of as high as 5000 Sm<sup>-1</sup> [24]. However, one of major drawbacks for the solvent mediated method is that, graphene sheets have a tendency to agglomerate and stack together. This tendency has been found to be persistent in spite of repeated sonication owing to van der Waals' forces of attraction. In order to avoid stacking, dispersing agents and surfactants widely used before sonication. Since no chemical modification has been done, the obtained graphene sheets are of very high purity and an yield of as high as 5.3 milligrams per mL are obtained. In addition, this method comes in the category of green method, as no harmful chemicals are used [25]. Stabilizing agents used in this method are sodium dodecyl sulphate, sodium dodecyl benzene sulphonate, triethanolamine, cetyl trimethyl ammonium bromide, as they do not allow the graphene layers to stack together [25]. Sonication method has been reported using 3D hydrogel as a support for "microbe immobilization" and as a biosensor to obtain graphene oxide suspension. In a typical procedure 2mg per milliliters of graphene oxide suspension to neutral red which was sonicated for 8-10 mins? The solution was heated in a Teflon lined autoclave for five hours at 180 °C. The solution, after being cooled, filtered and washed with de-ionized water, subsequently used for characterization [26]. The de-stacking of the sheets and hence the stabilization takes place by taking advantages of pi-pi interactions. Aromatic compounds, in this regard, can be used for prevention of graphene sheets [27,28]. In some instances, the energy of interfacial tension between two liquids (immiscible) can be utilized to prevent stacking. Water and heptane can be used for this purpose and they can lead to the formation of highly transparent graphene sheets having good electrical conductivity. Graphene is coated with on glassy surfaces with the help of chemical agents like chlorosilanes [28], which leads to formation of high-quality graphene sheets useful for solar panel formation, electronics as well as optoelectronics. The pH of the solution can be modified by addition of proper alkali such as sodium hydroxide, hydrazine etc. The solution is subsequently sonicated for 2 hours at a solution temperature of 70 °C [3]. Among the different chemicals, hydrazine reacts effectively with graphene oxide in presence of sonic radiation and removes epoxide as well as hydroxyl groups due to oxidation [3].

- 8. Methods Based upon Radiation:** For production of graphene for a very short period of time, radiation-based method is used, though the yield is very low. However, this method is highly favored as high quality of graphene can be obtained. But in industrial purposed this method is not favored as there is great deal of radiation concerns. In such processes, graphene oxides, with the help of the electron beams, reduced to graphene.

Here, graphene oxide is taken as in water dispersion along with isopropyl alcohol in a sealed bag. To this electron beam is provided at 2 MeV and 10mA [29,30]. Thus, reduced graphene sheets are then separated by centrifugation washed and dried. In some of the cased laser scribing is also used in a manner similar to pyrolysis. This technology has wide applicability in piezoelectric patches to harvest energy from mechanical movements and hence for devising camouflage uniforms [31]. Apart from laser Xenon flash, UV light, pulsed laser, femtosecond laser etc has been successfully used [32, 33].

- 9. Ball Milling Process:** One of the subcategories of mechanical exfoliation is ball milling which is being used for formation of homogeneous mixture as well as reduction of the particle size. Such scheme of reduction of the particle size has been explored by scientists to exfoliate the graphene sheets in graphite by chemical or magnetic assistances as well as solvent assistances [34-35]. In magnetic procedures, the magnets help in separation of metallic particles present in the precursor. Whereas the chemical technique assists in restacking prevention using pi-pi interactions [36,37], with high yield of production. Here graphene sheets of very high surface area are achievable.

## II. DIFFERENT BOTTOM-UP APPROACHES

- 1. Epitaxial Growth on Silicon Carbide (SiC):** For epitaxial growth of graphene silicon carbide is used as substrate which is supposed to be very much ideal for uses in circuits as well as transistor components [38-40]. In this method very thin graphene sheets can be obtained. The size can range as low as fifty micrometers. In typical procedure, silicon carbide is heated above 1100 centigrade to produce epitaxially grown graphene. This method is also suitable for production of graphene flakes; however, their size depends on the size of silicon carbide wafers. The surface properties of graphene such as its mobility, thickness as well as charge carrier density can be influenced by the surface itself of silicon carbide [41], producing very weak autolocalized graphene [42]. It was noticed that, in a way similar to the peel off method, this method producing epitaxially grown graphene has very much high temperature independent mobility [13], mass less “Dirac fermions” [36]. However, in “multi-layered” “epitaxial graphene”, cohesive forces exist among the layers owing to weak van der Waals forces, which however do not impact the electronic movements, which is related to the “symmetry of interlayer interactions” [44]. Such a phenomenon is not observed in bulk graphite. It has been seen that a two-inch wafer of silicon carbide can cut off frequency around 100 giga hertz [45]. Though this method produces high quality graphene, but it requires very high production cost as silicon carbides are expensive.
- 2. Method Involving Dry Ice:** In this method, graphene obtained by burning magnesium ribbon in a bowl containing dry ice which is covered by other dry ice. Here, magnesium completely burns in presence of carbon dioxide and the residue is kept on stirring for 24 hours in hundredmilliliters of acidic solution. As both magnesium and its oxide are soluble in water, thus the mixture is filtered easily and can be washed with distilled

water. Subsequently this is dried in vacuum at 100 degrees. Resulting in a yield of more than 90% [46].

- 3. Growth from Metal-Carbon Melts:** Here a carbon source is heated at high temperature, which is taken in contact to a transition metal, which subsequently leads to melting of the metal. Subsequently the carbon starts dissolving in the molten metal, and here the temperature is lowered to decrease the solubility. This led to the precipitation of excess carbon. This is then skimmed off, producing carbons in different forms such as graphene, thick graphite as well as single graphene layers. Here the transition metal chosen often successfully, is nickel [34]. However, when Ru and Ir are used the quality of graphene produced is not up to the mark [35]. Among other synthesis techniques of this variation, CVD is widely in use. Here a film of Ni is heated higher than 900 degrees under inert atmosphere of argon along with traces of methane gas. The purpose of methane gas is to let the carbons present in it to be absorbed on the surface of the film. After a specific time, the methane supply is cut off and the system is cooled down, by which the carbon diffuses out of the nickel surface, forming graphene sheets [36]. Copper also has successfully been used instead of nickel at low pressure and high temperature, as atmospheric pressure could lead to multilayer deposits of graphene on both of these metals [37]. In such methods large films of graphene can be deposited [87, 90, 91]. Other gases such as ethane and propane, leads to coating of bilayers on these metals which could be ascribed to their molecular structure owing to high carbon concentration.
- 4. Technique of Deposition:** Owing to their practical applicability there have been a great number of methods reported on “deposition-based methods” for graphene synthesis [22]. Thin films are known to be produced by “chemical vapor deposition techniques” [10] and owing to the large sizes of such films, they are suitably made applicable to smart windows, flexible LCD, solar cells, OLED as well as touch screen devices. Good qualities of large films of graphene can be produced by “chemical vapor deposition techniques” [5, 36, and 38]. Through spin coatings, graphene sheets obtained which are “nanotube-reinforced”. In addition, highly flexible, conductive a stronger graphene is obtained by using functionalized Dodecyl substrate “single wall carbon nanotubes” using spin coating and subsequent annealing. In typical methods, substrate solution of solution “DFSWCNT” and “trichloromethane” has to be dispersed on copper foil which has to be previously heated. Subsequently it needs to be annealed for more than 1000 deg but below 1100 degree for 15 minutes under the flow of hydrogen and argon gas. The chamber pressure is maintained about 930 pascals. The samples then required to be removed and subsequently cooled to room temperature [42,43]. As an inexpensive method for deposition of graphene in different substrates, supersonic sprays are widely used. This method improves the quality of graphene as it is produced with little or no defects as confirmed by “ID/IG ratio” less than 0.22. [44]. In this method the droplets are subjected to “supersonic acceleration” leading to kinetic spray deposition [22]. In another method called “dip coating” graphene oxide is deposited on silica or quartz which subsequently reduced to graphene through help thermal treatment under argon or hydrogen atmosphere. This results in graphene sheets with proper control of thickness [40], which is useful for production of optoelectronic applications and solar panels. The graphene thus produced has proper optical transparency and good conductivity also thermal and chemical stability. Graphene sheets can also be produced by “vacuum filtration” through the membranes of cellulose ester having pore size below 30 nanometers. When the solvent is drained, the graphene oxide forms a layer on the

cellulose. As the pores are blocked by graphene oxide, further passage of solvent is blocked, resulting in suspension of remaining graphene oxide to other pores. This acts more or less as a self-regulating system. Moreover, the thickness can be tamed by control of the solution concentration. When the filtration is finished, the cellulose can be dissolved by acetone. The graphene oxide obtained thus can successfully be used in lithography. The graphene oxide film thus obtained has to be reduced to graphene film through different reductants [44-46]. For an appropriate result the combined effect of vapor of hydrazine and low temperature in annealing is used [47, 48]. A layer-by-layer deposition is achieved by a research group, producing a multilayer film of graphene. Multilayer films could also be fabricated by dipping indium tin oxide coated glass slides in aqueous solution of “poly (diallyldimethylammonium) (PDDA)”. Thus; produced films have a surface positive charge. The films then washed in ultra-pure water and dried under continuous flow of an inert gas. The positive charged substrates are then immersed in solution of “poly (sodium 4- styrenesulfonate) modified graphene sheets (PSSGS)” for a period of 30 minutes with subsequent washing and dried in oven, thus producing a uniform layered substrate. It is known that the intensity ratio of “ID/IG” measures the degree of disorderness and average size of hybridized carbon domains and thus the value can be used to calculate the crystallite size of graphene as well as graphite. Lower the structural defects, smaller the “ID/IG” value

### III. CONCLUSIONS

The immense importance and fame of graphene is because of its advanced and useful properties and its potential towards formation of high-performance composites. High quality graphene needs upscaling which is great challenge to the researchers as this method is not suitable for its production (high quality graphene). Different top down and bottom approaches have been used by scientists and provides good quality fabrication of graphene sheets. The bottom-up approaches such as “CVD”, gives high control over quality and thickness however is not suitable for industrial preparation. However, the graphene thus produced in such a procedure is suitable for different advanced field applications like “touch screen LCD” “OLED”, “solar panels”, etc. Through “top-down approach” involves the breakage of the graphene precursor such as graphite, graphene etc. Different methods of fabrication have been utilized for such goals shearing; provide easy and “scalable” approach. The main challenge and difficulty of control and maintenance of consistence properties which is of vital importance in industrial scale production. However, a particular dimensioned graphene may not be suitable to fit all purposes and proper tuning of the quality as well as size in of great importance, which is the driving force of evolution of different methods of synthesis of graphene. And graphene synthesized by different procedures is suitable for use in different applications. As the new and advanced methods of fabrication is becoming increasingly interesting, thus it is hoped that in near future we will achieve a fair and justified balance between “quality” and “scalability”.

### IV. ACKNOWLEDGEMENT

The author is very much thankful to Centurion University of Technology and Management for providing necessary support and platform to carry out research.

## REFERENCES

- [1] J. Gao, M.E. Itkis, Yu A, Continuous Spinning of a Single-Walled Carbon Nanotube–Nylon Composite Fiber *J Am Chem Soc* vol. 127, pp. 3847–54, 2005.
- [2] P. Kulpinski Cellulose fibers modified by silicon dioxide nanoparticles *J. Appl. Polym. Sci.* vol. 98, pp. 1793–8, 2005.
- [3] S. Kedem, J. Schmidt, Y. Paz, Composite polymer nanofibers with carbon nanotubes and titanium dioxide particles *Langmuir* vol.21 pp5600–4, 2005.
- [4] G. Ren, Z. Zhang, X. Zhu, Mechanical properties of graphene and graphene-based nanocomposites *Compos Part A: Appl Sci Manuf* vol.4, pp. 157–64, 2013.
- [5] S. Stankovich, D.A. Dikin, G.H. Dommett, Graphene-based composite materials *Nature* vol. 442, pp.282–6, 2006.
- [6] A.V. Raghu, Y.R. Lee, H.M. Jeong, Review of functionalization, structure and properties of graphene/polymer composite fibers *Macromol. Chem. Phys.* Vol. 209, pp.2487–93, 2008.
- [7] P. Fan, L. Wang, J. Yang, Effect of Graphene Nanoplates on Phase Structure and Electrical Properties of Epoxy/Polyetherimide Composite *Nanotechnology* vol. 23, pp.365-702, 2012.
- [8] R. Verdejo, M.M. Bernal, L.J. Romasanta et al. Graphene filled polymer nanocomposites *J Mater Chem* vol. 21, pp.3301–10, 2011
- [9] H. Kim, Y. Miura, C.W. Macosko. Graphene/polyurethane nanocomposites for improved gas barrier and electrical conductivity *Chem. Mater.* Vol. 22, pp.3441–50, 2011.
- [10] E.-Y. Choi, T.H. Han, J. Hong, Noncovalent functionalization of graphene with end-functional polymers *J. Mater. Chem.* Vol. 20, pp.1907–12, 2010.
- [11] M.A. Rafiee, J. Rafiee, Z. Wang, et al. Enhanced mechanical properties of nanocomposites at low graphene content *ACS Nano* vol. 3, pp. 3884–90, 2009.
- [12] P. Sutter, J.T. Sadowski, E.A. Sutter. Chemistry under cover: tuning metal-graphene interaction by reactive intercalation *J. Am. Chem. Soc.* Vol.132 pp. 8175–9,2010.
- [13] Z. Liu, J.T. Robinson, X. Sun, PEGylated Nanographene Oxide for Delivery of Water-Insoluble Cancer Drugs *J. Am. Chem. Soc.* Vol. 130, pp. 10876–7,2008.
- [14] X. Yang, X. Zhang, Z. Liu, High-Efficiency Loading and Controlled Release of Doxorubicin Hydrochloride on Graphene Oxide *J. Phys. Chem. C* vol.112, pp.17554–8, 2008
- [15] J. Liu, L. Tao, W. Yang, Review of functionalization, structure and properties of graphene/polymer composite fibers *Langmuir* vol. 13, pp.10068–75, 2010.
- [16] J. Liu, J. Tang, J.J. Gooding. Strategies for chemical modification of graphene and applications of chemically modified graphene *J.Mater. Chem.* Vol. 22 pp. 12435–52, 2012.
- [17] D. Wei, Y. Liu, Y. Wang, Synthesis of N-Doped Graphene by Chemical Vapor Deposition and Its Electrical Properties *Nano. Lett.* Vol. 9, pp.1752–8, 2009.
- [18] S..Thakur, N. Karak Green reduction of graphene oxide by aqueous phytoextracts *Carbon* vol. 94, pp. 224–42, 2015
- [19] M.J. McAllister, J.-L. Li, D.H. Adamson, Single Sheet Functionalized Graphene by Oxidation and Thermal Expansion of Graphite *Chem Mater* vol. 19, pp. 4396–404, 2007.
- [20] H.M. Hassan, V. Abdelsayed, S.K. Abd El Rahman, Synthesis and structural characterization of separate graphene oxide and reduced graphene oxide nanosheets *J. Mater. Chem.* Vol.19, pp. 3832–7.2009
- [21] L. J .Cote, R. Cruz-Silva, J. Huang Flash Reduction and Patterning of Graphite Oxide and Its Polymer Composite *J. Am Chem. Soc.* Vol.131, () pp.11027–32, 2009.
- [22] Y.H. Ng, A. Iwase, A. Kudo, Reduced Graphene Oxide as a Solid-State Electron Mediator in Z-Scheme Photocatalytic Water Splitting under Visible Light *J.Phys. Chem. Lett.* Vol.1 () pp. 2607–12, 2010
- [23] S. Pei, H.-M. Cheng. Synthesis of Graphene Oxide (GO) by Modified Hummers Method and Its Thermal Reduction to Obtain Reduced Graphene Oxide (rGO) *Carbon* vol.50, pp. 3210–28, 2012
- [24] H.J. Shin, K.K. Kim, A. Benayad, Reduced graphene oxide produced by chemical and hydrothermal methods *Adv. Funct. Mater.* Vol.19, pp.1987–92, 2009.
- [25] Y. Zhu, S. Murali, M.D .Stoller, Carbon-based supercapacitors produced by activation of graphene *Carbon* vol. 48, pp. 2118–22, 2010.
- [26] D.R. Dreyer, S.Park, C.W. Bielawski, The chemistry of graphene oxide *Chem. Soc. Rev.* vol. 39 pp. 228–40, 2010
- [27] J. Liu, W. Yang, L. Tao, J. Thermosensitive graphene nanocomposites formed using pyrene-terminal polymers made by RAFT polymerization *Polym. Sci. Part A: Polym Chem* vol. 48 pp.425–33, 2010.



- [31] M.A. Rafiee, J. Rafiee, I. Srivastava, Fracture and fatigue in graphene nanocomposites *Small* vol. 6, pp.179–83, 2010
- [32] Y. He, N Zhang, Q. Gong, A Comparative Study on Properties of Cellulose/Antarctic Krill Protein Composite Fiber by Centrifugal Spinning and Wet Spinning *Carbohydr. Polym* vol.88, pp.1100–8, 2012
- [33] O.J. Yoon, C.Y. Jung, I.Y. Sohn, ADVANCES IN GRAPHENE-BASED MATERIALS AND THEIR COMPOSITES WITH FOCUS ON BIOMEDICAL APPLICATIONS *Compos Part A: Appl Sci Manuf* vol. 42, pp.1978–84, 2011.
- [34] [31] Y. Li, Q. Du, T. Liu, Methylene blue adsorption on graphene oxide/calcium alginate composites *Carbohydr. Polym.* Vol. 95 pp. 501–7, 2013
- [35] Y. Li, J. Sun, Q. Du, Effect of graphene oxide nanosheets on the physico-mechanical properties of chitosan/bacterial cellulose nanofibrous composites *CarbohydrPolym* vol. 102 pp.755–61. 2014.
- [36] M. Tian, L. Qu, X. Zhang, M. Tian, L. Qu, X. Zhang, *CarbohydrPolym* vol.111 pp.456–62, 2014.
- [37] L. Zhou, H. Liu, X. Zhang Preparation of hexene-functionalized graphitic nanoplatelets for effective interaction with Nylon 6 *J Mater Sci* vol.50 pp. 2797–805, 2015
- [38] X. Ding, Y. Zhao, C. Hu., Spinning fabrication of graphene/polypyrrole composite fibers for all-solid-state, flexible fibriform supercapacitors *J.Mater. Chem. A* vol.2, pp.12355–60, 2014.
- [39] M. Shateri-Khalilabad, M.E. Yazdanshenas Fabricating electroconductive cotton textiles using graphene *CarbohydrPolym.* Vol.96 pp.190–5, 2013.
- [40] C. Xiang, W. Lu, Y. Zhu, Carbon Nanotubes *ACS Appl. Mater. Interf.* Vol.4 pp.131–6. 2011
- [41] F. Yavari, M. Rafiee, J. Rafiee, Dramatic Increase in Fatigue Life in Hierarchical Graphene Composites *ACS Appl. Mater. Interf.* Vol.2 pp.2738–43, 2010
- [42] P.M. Ajayan, J.M. Tour. Materials science: nanotube composites *Nature* vol.447, pp.1066–8, 2007.
- [43] C. Lee, X. Wei, J.W. Kysar, Measurement of the elastic properties and intrinsic strength of monolayer graphene *Science* vol.321, pp.385–8, 2008.
- [44] V. Sa, K.G. Kornev Sharpening the surface of magnetic paranematic droplets *Carbon* vol. 49, pp.1859–68, 2011.
- [45] F. Ko, Y. Gogotsi, A. Ali, Preparation, properties and application of polyamide/carbon nanotube nanocomposites *Adv. Mater. (Weinheim, Ger)* vol. 15, pp.1161–5, 2003.
- [46] Armentano, M. Dottori, D. Puglia, Effects of carbon nanotubes (CNTs) on the processing and in-vitro degradation of poly(DL-lactide-co-glycolide)/CNT films *J. Mater. Sci: Mater Med* vol.19, pp.2377–87, 2008.
- [47] M Shateri-Khalilabad, ME Yazdanshenas. Fabricating electroconductive cotton textiles using graphene *CarbohydrPolym* vol. 96, pp. 190-195, 2013.
- [48] G. Yu, L. Hu, M. Vosgueritchian, Solution-Processed Graphene/MnO<sub>2</sub> Nanostructured Textiles for High-Performance Electrochemical Capacitors *Nano Lett* vol.11, pp.2905–11, 2011
- [49] J. Zhao, B. Deng, M. Lv, Graphene oxide-based antibacterial cotton fabrics *Vol 2 ;2:* pp. 1259–66. 2013
- [50] Z. Fan, C. Zheng, T. Wei, Analysis of electrical and thermal conductivities of polyethersulfone-graphite based hybrid nanocomposites *Polym. Eng. Sci.* vol.49, pp.2041–5. 2009.
- [51] B. Pan, G. Xu, B. Zhang, Mechanical and Tribological Properties of Graphene Modified Epoxy Composites *Polym. Plast. Technol. Eng.* Vol.51, pp.1163–6, 2012